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Abstract

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O. V. Starovskii and Yu. T. Struchkov

The Structure of Ditoluenechromium Iodide

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In the present work the structure of ditoluenechromium iodide* has been investigated. The substance crystallizes in the space group $J2/m$. The unit-cell parameters are: $a = 7.94 \pm 0.08$; $b = 6.77 \pm 0.07$; $c = 12.55 \pm 0.10$ Å; $\beta = 104°22' \pm 10'$; the number of molecules in the cell is $N = 2$. The measured density is 1.7; the calculated density is 1.83 g/cm^3. The cations and anions are located in special positions, determined from a Patterson series: coordinates of the iodine atom $00\frac{1}{2}$, of the chromium atom 000. The ditoluenechromium cation in the crystal has symmetry $2/m$, which immediately determines the general features of the cation configuration: prismatic, with the methyl groups in the trans position (Fig. 1).

Since the positions of the "heavy" atoms (iodine and chromium) are fixed, and, moreover, from the symmetry of the cation in the crystal the plane is known in which the carbon atoms of the methyl group and two atoms of the six-membered ring are located, we undertook the construction of a section of the difference electron-density series by the plane $x0z$. From this section the positions of atoms C_0, C_1, and C_4 were found (Fig. 2). Then sections of the difference series were constructed by several planes parallel to the plane $x0z$

Table 1

Coordinates of symmetrically independent atoms*

Atom	Relative coordinates x	Relative coordinates y	Relative coordinates z	Coordinates, Å x	Coordinates, Å y	Coordinates, Å z
J	0	0	1/2	0	0	6.275
Cr	0	0	0	0	0	0
C_0 (CH_3)	-0.243_8	0	0.182_0	-1.93_6	0	2.28_4
C_1	-0.076_6	0	0.147_6	-0.60_8	0	1.85_2
C_2	0.005_9	0.181_4	0.135_2	0.04_7	1.22_8	1.69_7
C_3	0.170_8	0.181_4	0.110_4	1.35_6	1.22_8	1.38_6
C_4	0.253_8	0	0.098_0	2.01_1	0	1.23_0
H_2	−0.0569	0.3195	0.1447	−0.452	2.163	1.816

Fig. 1. Structure of the cation $(CH_3C_6H_5)_2Cr^+$. The distance $CH_3 \dots C'_4$ for the ideal position of the CH_3 group in the plane of the six-membered ring is given in parentheses.

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Atom	Relative coordinates x	Relative coordinates y	Relative coordinates z	Coordinates, Å x	Coordinates, Å y	Coordinates, Å z
H_3	0.2336	0.3195	0.1010	1.855	2.163	1.268
H_4	0.3789	0	0.0791	3.008	0	0.993

* The coordinates of the hydrogen atoms were found on the assumption that they are located on the straight line connecting the center of the six-membered ring with the corresponding carbon atom at a distance of 1.08 Å from the latter.

at heights (coordinate y) close to the theoretical position of atoms C_2 and C_3. As a result, the coordinates of all carbon atoms were obtained, as given in Table 1.

* The crystals of ditoluenechromium iodide were kindly provided by V. M. Chibrikin, staff member of the Institute of Chemical Physics, Academy of Sciences of the USSR.

Figure 1 shows the configuration of the ditolylchromium cation, with interatomic distances indicated. The accuracy of the investigation is ±0.01 Å for C—Cr distances and ±0.03 Å for C—C distances. The Cr—C distance in the cation (2.08 Å) agrees, within the experimental error, with the analogous distances in dicyclopentadienylchromium (2.09 ± 0.03 Å) (1) and in dibenzenechromium (2.19 ± 0.1 Å) (2). At the same time, this distance, as is usual in sandwich compounds, is close to the sum of the covalent radii of chromium and carbon atoms (2.04 ± 0.05 Å) (3).

Fig. 1. Structure of the cation $(CH_3C_6H_5)_2Cr^+$. In parentheses is given the distance $CH_3 \dots C'_4$ for the ideal position of the CH_3 group in the plane of the six-membered ring.

As is evident from the present work, on going from the neutral "sandwich" to the cation, the metal—carbon bond length, i.e., also the type of this bond, practically does not change. True, so far the ditolylchromium cation can be compared only with dicyclopentadienylchromium, since, owing to strong torsional vibrations of the six-membered rings, the bond lengths in dibenzenechromium were found by a fitting method, i.e., only very approximately.

Unfortunately, because of the strong anisotropy of the thermal vibrations of the schematic electronic shift in the ditolylchromium cation

Figure 2: schematic electronic shift in the ditolylchromium cation

atoms, the accuracy in determining the carbon—carbon bond lengths (±0.03 Å) is apparently below the possible differences in the lengths of individual bonds in the carbon ring. The mean C—C bond length in the ring (1.42 Å) coincides with the length of the same bond in ferrocene (1.405 ± 0.045 Å) (4), ruthenocene (1.43 ± 0.02 Å) (5), and is somewhat greater than the bond length in benzene (1.38 Å) (6). The length of the C_0—C_1 bond (between the carbon atom of the methyl group and the ring atom bonded to it) is 1.49 Å, i.e., somewhat less than the length of a single bond in aromatic compounds (∼ 1.52 Å). Such a change can apparently be explained by the fact that, in the formation of bonds of the "sandwich" type, there is a withdrawal of π-electrons of the aromatic ring toward the central metal atom (which, in the case of the ditolylchromium cation, is intensified because of the positive charge on the chromium atom). In turn, such a withdrawal of π-electrons from the six-membered ring should cause some shift of the electrons of the methyl group toward the ring:

This effect is manifested in a certain decrease in the bond order of the C—C bonds in the six-membered ring (and, consequently, in a certain lengthening of these bonds in comparison with benzene) and in an increase in the bond order of the C—C bond between the carbon of the methyl group and the aromatic ring (i.e., in a decrease in the length of this bond). Such an electron shift should also somewhat reduce the positive charge on the chromium atom and cause the appearance of some effective positive charge on the organic parts of the cation.

As is evident from Fig. 1, the CH_3 group is displaced out of the plane of the carbon ring. This is evidently explained by the excessively small distance from the methyl group to the nearest atom C_4' of the other carbon ring (3.5 Å instead of the equilibrium distance 3.8 Å) (3). A compromise is probably achieved between a certain "compression" of the atoms, i.e.

with a shortening of the distance $CH_3 \cdots C_4'$ by $3.8 - 3.5 = 0.3$ Å and a distortion of the valence angle of the carbon atom C_1 by 4°.

Figure 3 shows a projection of the structure of ditoluenchromium iodide on the *ac* face, with the shortest intermolecular (more precisely, interionic) distances indicated. As was shown using diphenyliodonium borofluoride $[(C_6H_5)_2J]^+[BF_4]^-$ (7) as an example, intermolecular radii retain their usual values also in ionic structures with large organic ions. Therefore the usual values of intermolecular radii are not surprising also in the

Fig. 2. Section of the difference series by the plane $x0z$ (atoms J and Cr have been subtracted). Lines of equal density are drawn at intervals of 0.5 e/Å^3, starting from 0.5 e/Å^3.

structure of ditoluenchromium iodide (carbon 1.77 ± 0.05; hydrogen 1.19 ± 0.09;

Figure 2. Section of the difference series by the plane x0z (J and Cr atoms subtracted). Lines of equal density are drawn at intervals of 0.5 e/Å^3, starting from 0.5 e/Å^3.

Figure 3: Figure 2. Section of the difference series by the plane x0z (J and Cr atoms subtracted). Lines of equal density are drawn at intervals of 0.5 e/Å^3, starting from 0.5 e/Å^3.

iodine 2.03 ± 0.15; methyl group 1.98 ± 0.08 Å), although in both of these cases they describe not intermolecular but interionic distances.

The structure is formed by infinite dense layers in the planes $x0z$; $x\frac{1}{2}z$; $x1z$ $\cdots$The layers are not maximally dense: voids remain in them at the positions $x = \frac{1}{2}, z = 0$ and $x = \frac{1}{2}, z = \frac{1}{2}$. The voids are covered from above and below by ions of the upper and lower layers.

The superposition of layers occurs with maximum density. The packing coefficient, equal to 0.73, indicates a high packing density, which is also reflected in the large coordination numbers: each anion touches 6 cations, each cation—6 anions and 10 cations.

The principal feature of the crystal structure is the extremely simple type of ion packing. This structure is, as it were, an organometallic analogue of the NaCl structure. As in the latter, there is a very symmetrical environment of ions of one sign by ions of the other sign, with coordination number 6. Moreover, the iodine ions surrounding a given cation (and, conversely, the centers of the cations surrounding a given iodine ion) are located at the vertices of only a slightly distorted octahedron. These features of the structure of ditoluenchromium iodide, sharply distinguishing it from the structures of most other ionic organic compounds (for example, salts of amines or carboxylic acids), are explained by the high symmetry of the cation $(CH_3C_6H_5)_2Cr^+$ and by the closeness of its shape and, evidently, of the force field it creates to spherical.

It may be expected that other ionic π-complexes will also be characterized by the simplicity of the type of ion packing because of the high symmetry of the sandwich cations. This is confirmed by the results of our study of the structure of titanocene dichloride $[(C_5H_5)_2Ti]^{+2}Cl_2^-$. Crystals

of this compound belong to the space group $I2/n$ of the monoclinic system; unit-cell parameters: $a = 14.17 \pm 0.04$; $b = 6.50 \pm 0.02$; $c = 12.39 \pm 0.06$ Å; $\beta = 115 \pm 1°$; $N = 4$. The great similarity of this structure to the structure of ditoluenechromium iodide is noteworthy; the cell of $(C_5H_5)_2TiCl_2$ differs from the cell of $(CH_3C_6H_5)_2CrJ$, roughly speaking, only by a doubling of the period a and of the number of molecules, while the remaining parameters and the centering mode are preserved. This structure is an organometallic analogue of the typical ionic inorganic layered

Fig. 3. Projection of the structure of ditoluenechromium iodide on the *ac* face

Fig. 3. Projection of the structure of ditoluenechromium iodide on the *ac* face (distances in Å are indicated). The ions of the $x0z$ layer are shaded; the ions of the lower layer $x'1/2z'$ are light.

Figure 4: Fig. 3. Projection of the structure of ditoluenechromium iodide on the *ac* face (distances in Å are indicated). The ions of the $x0z$ layer are shaded; the ions of the lower layer $x'1/2z'$ are light.

(distances in Å are indicated). The ions of the $x0z$ layer are shaded; the ions of the lower layer $x'1/2z'$ are light.

structure of $CdCl_2$. The example presented once again confirms the far-reaching crystallochemical analogy between ionic inorganic structures and ionic organometallic structures with spherically symmetric ions (in particular, sandwich π-complexes).

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Institute of Organoelement Compounds
Academy of Sciences of the USSR

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